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# Mass spectrometric determination of deuterium by means of phosphine

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With 3 figures in the text

**Introduction.** The isotopic analysis of hydrogen by mass spectrometer is cumbersome and less accurate than that of other light elements where gaseous compounds were available. Usually hydrogen is introduced into the spectrometer (1). The chief difficulties in the measurement were the competition of the ions $H_3^+$ with the essential ions $HD^+$ on mass number 3, a perceptible discrimination of the spectrometer because of the relatively large differences in weight of the molecules and ions in question, a certain background in the spectrometer on these mass numbers and finally the exchange of hydrogen with that which is present as impurity in the spectrometer. Methane, ammonia and water are unsuitable because of the interference of other rare heavy isotopes. Moreover, the critical ions for these compounds are found on mass numbers where a certain background always exists. Ammonia and especially water will also be considerably adsorbed and give rise to a strong "memory" of the mass spectrometer.

Some experiments with phosphine were made by the author in 1948. These were finally suspended, however, because of annoying adsorption effects. Meanwhile, advances have been made in the elimination of adsorption which occurs during mass spectrometric analysis of strongly polar compounds (2), and also a new and somewhat improved mass spectrometer has been built in our own laboratory (3). Therefore it was found worth while to resume this work. Due to external circumstances, it has been impossible to carry these experiments as far as necessary to arrive at a well elaborated procedure, but, nevertheless, an account will be given as an aid to eventual future research.

**Earlier work on phosphine.** Aston (4) investigated the isotopic constitution of phosphorus by means of phosphine. He was unable to detect the very faint line on m. n. 35, and therefore reached the conclusion that phosphine consisted entirely of $P^{31}H_3$. Presumably mass spectrometers are also used for the measurement of phosphine in industrial gases (5).

Exchange reactions of normal and of deuterated phosphine with deuterium and protium have been studied spectroscopically by Bolland and Melville (6). Their paper is also of interest because of the sampling techniques described therein.

**Preparation of phosphine.** It was considered that the samples of hydrogen to be analyzed, for the most part, would be available as water. The quantities might be

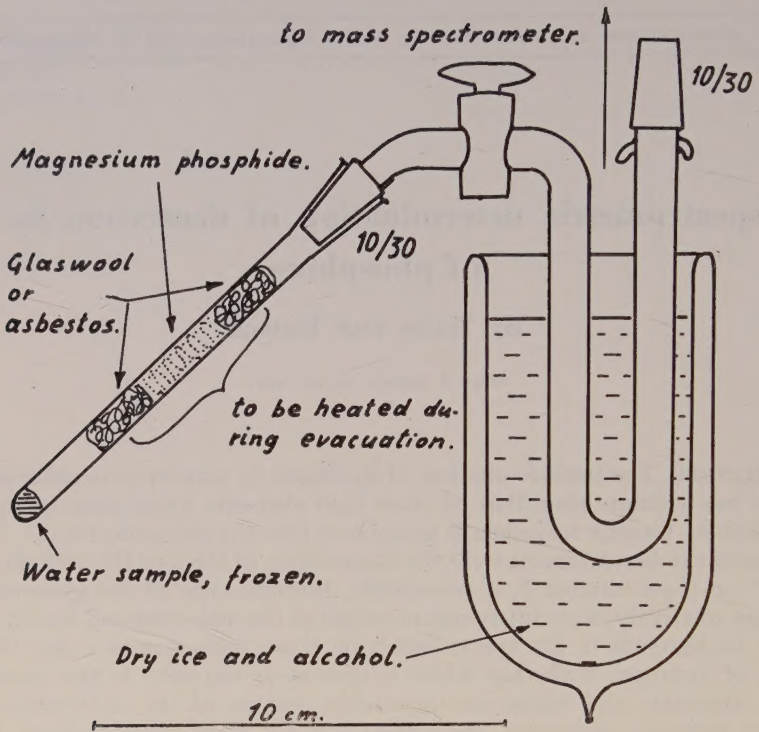

Fig. 1. Preparation of phosphine.

very small if originating e.g. from biological tracer research. Therefore the method adopted was to pass the vapour of a few drops of water over magnesium phosphide (or calcium phosphide (6)). The apparatus used, illustrated in Fig. 1, was connected directly to the gas inlet system of the mass spectrometer. Any diphosphine evolved is retained in the trap. Any hydrogen, however, can only be retained through a fractional distillation of phosphine by means of liquid air. Fortunately, this was unnecessary.

Phosphine is a very poisonous gas which ignites spontaneously on contact with air. The absorption by water is small and the absorption in a vacuum system is at most not greater than that of carbon dioxide.

**Characteristics of the mass spectrometer.** A 180° pyrex tube was used. The internal metal parts were made of copper-plated Nichrome V and copper, all of which were lightly gold-plated. Evacuation was accomplished by means of a 3-stage pyrex diffusion pump using Octoil-S. A dry-ice trap was inserted. The leak consisted of a "pinhole" inside a 3 mm pyrex tube and was located 1 cm from the ion source. A tungsten ribbon was used as electron emitter. The energy of the electrons was 70 eV. The pressure of phosphine in the inlet system was usually 15 mm Hg. The tube was not heated during operation.

**Mass spectra of phosphine.** They have usually been obtained by means of a recorder. Fig. 2 shows a spectrum resulting from tap water and Fig. 3 another ob-

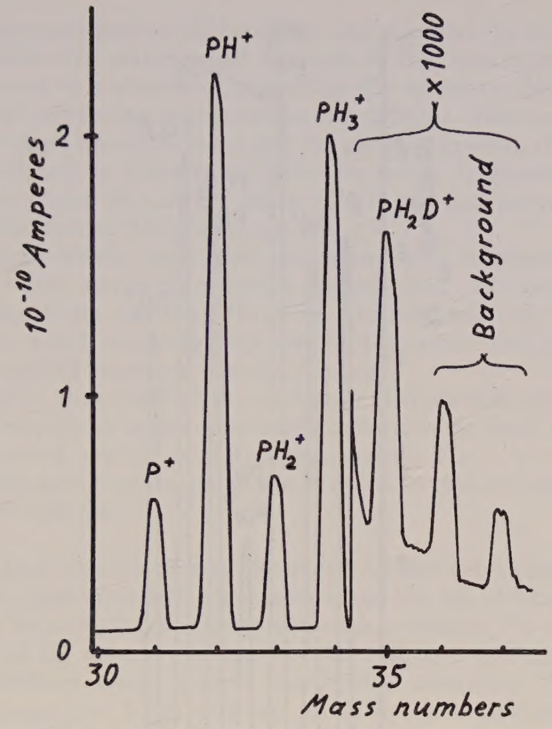

Fig. 2. Sample made from tap water.

tained with the highest concentration of deuterium oxide which was available. The relative heights of the peaks on the mass numbers 31, 32, 33 and 34 in Fig. 2. depend to some degree on the individual mass spectrometer or tube used. Differences up to 30 % have been observed. The heights were not very constant and could be reproduced only within 5 %. A very small trace on m.n. 62 and still smaller ones on 63 and 64 may be ascribed to diphosphine.

If deuterium is present in small concentrations only, it manifests itself on m.n. 35, as is shown in Fig. 2. It is a favourable circumstance that this mass number usually shows only a very slight background or none at all. It is smaller than that of adjacent mass numbers, and in the present case amounted to only 1/12 of the peak height in Fig. 2. The neighbouring peaks on m.n.'s 36 and 37 are the ever-present carbon impurities.

The ratio of hydrogen to deuterium obviously equals three times the ratio (34)/(35), the 35-peak having been corrected for the background. The reproducibility of this ratio for tap water was about 5 % in the present experiments.

The deuterium oxide which produced the spectrum in Fig. 3 was nominally 99 %. However, the sample was no longer pure and may also have caught some protium during the preparation of the phosphine and later by exchange in the spectrometer. The ratio (36)/(37) indicates 26 % protium and 74 % deuterium. Investigation was made as to whether the pattern in Fig. 3 could be ascribed to the four partial spectra from the different kinds of phosphine molecules which are present in the statistical equilibrium, and which are dissociated and ionized in accordance with the pattern

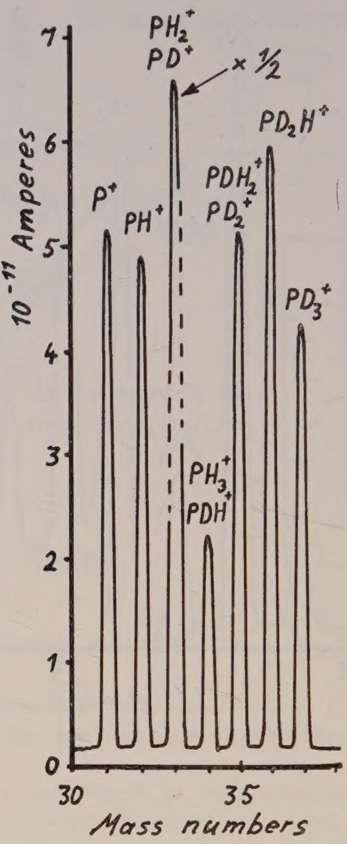

Fig. 3. Sample very rich in deuterium.

of $PH_3$ in Fig. 2. However, there was a surplus by 40 % on m.n. 31, by 20 % on m.n. 33, and by 100 % of $PH_3$. This, of course, makes the use of the ratio (36)/(37) somewhat questionable for *absolute* determinations. Background corrections, however, were not necessary on these mass numbers.

**Adsorption, hydrogen exchange and »memory».** In addition to tap water and the deuterium oxide already described, water samples were used which held 1/10 000, 1/1 000, 1/100 and 1/10 parts of 99 % deuterium oxide in addition to their natural contents. The resulting measurements showed only approximately 60 % of the expected deuterium content. Samples of tap water run alternately showed somewhat increased deuterium content.

Inside the mass spectrometer tube an adsorption of phosphine takes place, and a certain exchange of hydrogen may occur in the adsorbed state as well as in the gaseous. Tank hydrogen was added in equal quantities to the various samples of phosphine and the spectra recorded before and after the addition were examined. *No significant differences were detected, even for the deuterium oxide sample.* This indicates that no ion $PH_4^+$ was formed, which would have interferred with the deuterium measurement just as $H_3^+$ interfers, and also that the exchange of hydrogen in the gaseous state was rather small (at least in that particular tube),

After the removal of a sample of phosphine the spectrum decreased to tenths of one percent of the initial value within one or two minutes. However, if approximately 20 mm Hg of hydrogen was introduced into the gas inlet system, the residual spectrum was raised immediately to about seven times its value. It decreased again after the removal of the hydrogen to a lower value than it had had previously. This should explain the mechanism of the "memory."

These latter experiments were also performed with a phosphine sample made from deuterium oxide and with a freshly baked tube. The residual spectrum indicated a *high* deuterium content. However, the admission of tank hydrogen provoked a spectrum which was definitely *poor* in deuterium, and after removal of the hydrogen, the residual spectrum remained poor.

Thus it is evident that most of the exchange of hydrogen takes place in the adsorbed phase. Probably it is the dissociated molecules (or ions) which are the more effective. This would explain why the spectrum in Fig. 3 is irregular, as stated. Perhaps a catalytic action of the materials in the tubes takes place, which causes the differences in the spectra.

**Conclusion.** It is possible to use phosphine for the determination of deuterium. The very suitable mass numbers which also make the use of NIER's double collector possible (1) offer an advantage if compared with hydrogen. No complication similar to the formation of $H_3^+$ occurs. Adsorption and hydrogen exchange are troublesome, however, and therefore should deserve the greatest attention. The accuracy is the same as for hydrogen ($\approx 5\,\%$), and can probably be somewhat increased.

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